II. *The Electrical Conductivity and Luminosity of Flames containing Salt Vapours.*

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When the vapour of an alkali salt is present in a Bunsen flame the vapour becomes luminous and also increases the electrical conductivity of the flame. The fraction of the salt molecules which are luminous is probably very small, and unless the concentration of the salt vapour is very small the fraction of the salt molecules which are charged electrically, or are ionised, is also very small.

Any particular salt molecule enters the flame at the bottom and moves up the flame with the velocity of the flame gases which is of the order of 200 cm. per second. The molecule is therefore in the flame for only a small fraction of a second, but this time interval is probably long enough for a state of equilibrium to be established between the several states in which the molecules can exist. For example, in the case of sodium chloride there is probably an equilibrium between $NaCl$, $NaOH$, Na_2O, Na, H_2O, HCL, and possibly other bodies such as CO, CO_2, and Na_2CO_3.

Each sodium atom must exist in the flame successively in different states and will, on the average, exist in each state a definite fraction of the time it is in the flame. Of course the time interval may not be long enough for every atom to pass through all the possible states, but on the average there will be a definite fraction of all the sodium atoms in each possible state. In some of the possible states the atoms may be luminous during the whole or during only a fraction of the time the atoms are in those states, and during the whole or a part of the time the atoms are in any state they may be positively charged and so form ions. The object of the experiments described in this paper was to obtain information about the relative numbers of the atoms in the different possible states, especially the luminous state and the positively-charged state, and about the nature of the luminous state and the charged state.

In an electric field the charged molecules or ions tend to move with a definite velocity proportional to the electric intensity. This velocity will be denoted by kX, where k is the velocity due to unit field and X the field strength. The average velocity, over a long time, of any particular metal atom due to the field will be fkX, where f denotes the fraction of the time during which the atom is in the positively-charged state. The time during which the atoms are in the flame may not be long enough for each atom to pass through all the possible states, so that actually only

a fraction of the atoms may be moved by the field.   The average velocity of all the atoms due to the field will be equal to fkX, but only a few atoms may actually move. If this happens, the velocities of those atoms which are moved by the field will lie between zero and kX.   A few atoms may be ionised all the time they are in the electric field and these will have the maximum velocity kX.

If the average life of an ion is small compared with the time the molecules are in the electric field, then all the molecules will move with the velocity fkX, but if the average life is not small compared with the time the molecules are in the field, then the velocities will vary between zero and kX, but the average for all the salt molecules will still be equal to fkX.

The rest of this paper is divided into the following sections :—

    I. Motion of luminous salt vapours in flames due to an electric field.
    II. Velocity of the positive ions of salt vapours in flames.
    III. Relation between luminosity and conductivity of salt vapours in flames.
    IV. Variation of the conductivity with the concentration of the salt vapour.
    V. Relative conductivities due to salts of different metals.
    VI. Summary and conclusion.

PART I.—MOTION OF LUMINOUS SALT VAPOURS IN FLAMES DUE TO AN ELECTRIC FIELD.

LENARD[*] found that the luminous streak of vapour from a salt bead in a flame could be deflected towards the negative electrode by a horizontal electric field.   This deflexion has since been examined by ANDRADE.[†]

The flame itself is also attracted by the negative electrode.   ANDRADE observed the deflexion of the edge of the flame nearest to the negative electrode and subtracted this from the deflexion of the luminous streak to get the deflexion of the streak relatively to the flame gases.   He found the deflexion of the flame to be about half that of the streak.   I have repeated these experiments and found it difficult to be sure that there was any real difference between the deflexion of the flame and that of the streak of salt vapour.   The edge of the flame is not sharply defined, and when salt was put in it seemed to me to change the deflexion of the edge of the flame if the vapour extended to the edge.   I also found that in a flame which was little if at all deflected, there was little, if any, deflexion of the salt vapour, although a strong electric field was used.

These preliminary experiments suggested that the deflexion of the luminous streak of salt vapour might be due to the deflexion of the flame as a whole, and not to a relative motion of the luminous salt molecules, through the flame, due to the electric field.

* 'Ann. d. Physik,' 9, 3, pp. 642–650, Oct., 1902.
† 'Phil. Mag.,' June, 1912, and July, 1912.

On the other hand, it was found that when the electric field was strong enough to cause a great increase in the current, that is, when an arc discharge began to form, then luminous salt vapour appeared between the streak and the negative electrode; the negative electrode, if in the flame, emitted a stream of luminous salt vapour. The intensity of the luminosity between the streak and the negative electrode was much less than in the streak itself. This suggested that, while the luminous molecules in the streak were not deflected, positive ions were moving out of the streak towards the negative electrode and that these ions could form luminous vapour; these last results are in agreement with some of those of ANDRADE,* who showed that positive
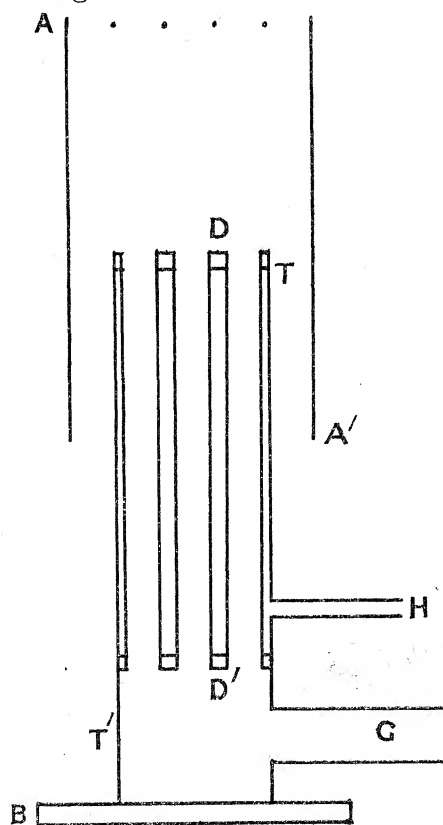
Fig.1.
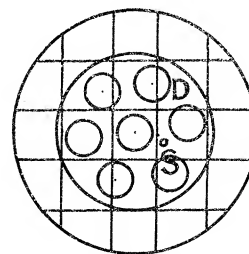
Fig.2.

ions from a streak when deposited on the negative electrode form luminous vapour. This fact was also previously observed by the writer.†

It was therefore decided to attempt to measure the relative motion of the luminous salt vapour and flame gases due to an electric field by a new method which seemed to be capable of giving more reliable results than those previously used.

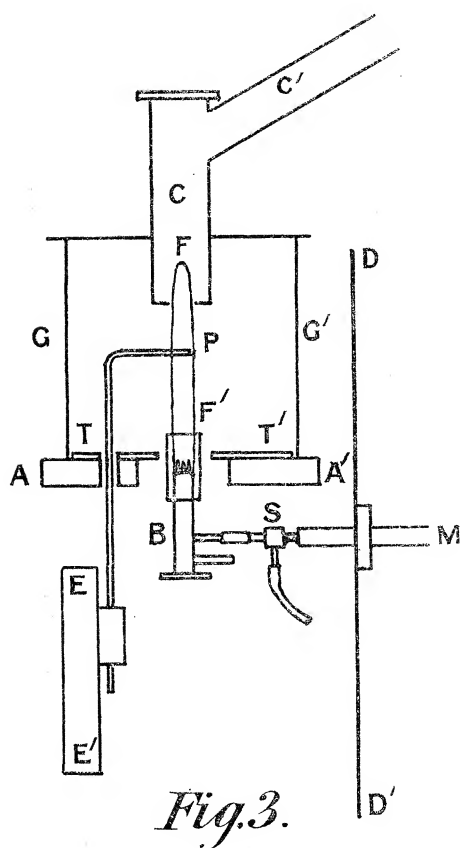The flame used was a Bunsen flame formed by burning a mixture of gasolene vapour and air from a special burner.

Fig. 1 shows a vertical section of the burner, and fig. 2 the top of it as seen from

* 'Phil. Mag.,' July, 1912.
† 'Proc. Royal Institution,' Feb. 12, 1909.

above. A brass tube, TT', about 3 cm. in diameter and 15 cm. long was soldered to a base plate, B. At D and D' brass disks were fitted tightly into the tube, TT'. Each of these disks had seven holes bored in it as shown in fig. 2, and seven parallel brass tubes connected the holes in the lower disk, D', with the holes in the upper disk, D. The mixture of gas and air entered through the side tube, G. The flame had seven sharply defined inner cones. The upper part of the burner was surrounded by a brass tube, AA', about 4·5 cm. in diameter, supported by three small brass blocks not shown in the figure.

A grating formed of ten platinum wires was fixed across the tube, AA', about one millimetre from its upper end. This grating was heated bright red hot by the flame and formed one of the electrodes. A mixture of air and spray of a salt solution entered the burner through a second side tube, H, which led into the space between the seven tubes. This mixture entered the flame through a small hole, S, in the upper disk, D, and produced a streak of salt vapour extending from S to the top of the flame. The air and spray entered H through a stop-cock which was ·rapidly opened and closed by means of an electric motor. The streak of vapour was therefore not continuous, but consisted of a series of puffs of vapour moving up the flame. The amount of salt in each puff could be varied by adjusting the pressure of the supply of air and spray. It could be diminished till the puffs were only just visible or increased till they were intensely luminous.

Fig.3.

The shaft of the motor carried a disk having four equidistant openings near its circumference. The stop-cock was opened four times during each revolution of the motor. The flame could be observed through the rotating disk so that it was then seen as many times per second as the stop-cock was opened. The puffs of salt vapour were then seen in the flame apparently stationary in a series of nearly equidistant positions one above the other. Fig. 3 shows the apparatus used. B is the burner and FF' the flame. S is the stop-cock through which the air and spray entered, and DD' the rotating disk carried by the motor shaft, M. AA' is a wooden base covered with a sheet of asbestos, TT'. GG' is a glass cylinder resting on the wooden base. The top of the cylinder is covered by a brass plate in the centre of which is fixed a vertical brass tube, C, which, with a tube, C', formed a chimney up which the gases from

the flame were led out of the room. The lower end of the tube, C, was fitted with a brass disk having a hole in it about 4 cm. in diameter, which was covered with a platinum wire grating like the one above the burner, B. At P a fine platinum wire was stretched horizontally across the flame perpendicular to the plane of the paper. This wire was carried by a glass tube which was supported on a slide, EE', so that the wire could be moved up and down along the vertical axis of the flame. The slide was provided with a millimetre scale and vernier. The potential difference between the wire, P, and the burner grating could be measured with an electrostatic voltmeter.

The tube, C, and the upper grating were usually connected to the earth, through a galvanometer, and the burner, B, and lower grating could be connected to a battery of 1800 dry cells, giving up to 2700 volts. In this way a vertical electric field could be maintained in the flame between the upper and lower gratings.

Let v denote the upward velocity of the flame, n the number of puffs of salt entering the flame per second, x_1 the height of a puff as seen through the rotating disk and x_2 the height of the next puff higher up. In the absence of an electric field the puffs simply move up with the flame so that

$$v = n\,(x_2 - x_1).$$

The heights of the puffs could be measured by adjusting the wire, P, so that it coincided with their tops or bottoms and reading the vernier on the slide, EE'. About three puffs were visible when the number of puffs was rather over 100 per second.

The puffs were equidistant showing the velocity of the flame to be sensibly uniform. It was found that $x_2 - x_1$ was nearly 3 cm. when N was equal to 100 per second. The velocity of the flame was therefore about 300 cm. per second and could be determined to within two or three per cent. without difficulty. The gas and air supplies to the flame were carefully regulated, and the gas and air were well mixed before they entered the burner. The burner gave an exceptionally steady and only slightly conical flame in the space between the wire gratings.

Let k denote the velocity of a luminous salt molecule in the flame due to an electric field of unit strength. We have

$$dx' = (v - k\mathrm{X})\,dt,$$

where x' denotes the height of the molecule above the lower grating, X the electric force reckoned positive when directed downwards, and t the time. Also in the absence of an electric field let

$$dx = v\,dt,$$

where x denotes the height of the molecule in this case.

Hence

$$dx - dx' = \frac{k}{v} X\, dx,$$

which gives

$$x - x' = \frac{k}{v} \int_0^x X\, dx.$$

But $\int_0^x X\, dx$ denotes the potential difference between the lower grating and the point a distance x higher up. Let this potential difference be denoted by V so that

$$k = v\,(x - x')/V.$$

Here $x - x'$ is the distance through which a puff of salt appears to be moved downwards, as seen through the rotating disk, when the lower grating is connected to the battery.

Since $v = n\,(x_2 - x_1)$ we have

$$k = \frac{n\,(x_2 - x_1)\,(x - x')}{V}.$$

If the puffs contain much salt vapour they have a greater conductivity than the rest of the flame so that the electric field will be less in the puffs than in the rest of the flame. In this case the salt inside the puffs will not be acted on by the whole of the potential fall, V, so that the deflexion of the puffs will be smaller than that represented by the equation just given. In the case of sodium and strontium salts, which have small conductivity and intense luminosity, it was possible to observe the puffs when the amount of salt in them was not enough to change the conductivity appreciably so that with these salts no error could be produced by the conductivity of the puffs. The fact that the conductivity with small amounts of these salts was not appreciable was shown by measuring the current with the stop-cock open all the time so as to get a continuous streak of the salt vapour. With small amounts of the salts the current was not increased by the salt more than 50 per cent. With the apparatus described it was found that the puffs of salt vapour did not appear to move at all when the battery was connected or disconnected. A motion of 0·5 mm. could have been detected, and V was increased to over 2000 volts in the case of some salts. This shows that k was less than

$$\frac{100 \times 3 \times 0·05}{2000} = 0·0075 \text{ cm. per second per volt per centimetre.}$$

Salts of sodium, strontium and potassium were tried and no deflexion of the puffs of vapour could be detected in any case. The amount of salt in the puffs was varied as much as possible in each case. With sodium and strontium V was increased to over 2000 volts, but with potassium it could not be raised above about 1000 volts without an arc striking between the electrodes. With sodium and strontium in

small amounts and large potentials the fall of potential was nearly uniform, but with potassium it nearly all occurred near the lower negative electrode.

It was found that if the tube, AA′ (fig. 1), carrying the lower grating was removed and the burner itself used as the lower electrode then the puffs of salt were deflected downwards when the burner was charged negatively. The deflexion was about 0·5 cm. for 1000 volts in the case of all salts.

This gives

$$k = \frac{100 \times 3 \times 0\cdot5}{1000} = 0\cdot15 \text{ cm. per second per volt per centimetre.}$$

Charging the burner negatively when the tube, AA′, was removed depressed the inner cones of the flame and caused the flame to broaden out slightly just above the burner. Evidently the electric field retarded the upward motion of the flame and so produced the downward deflexion of the puffs of salt vapour. When the burner was charged positively no deflexion could be detected. The tube, AA′, and platinum grating were therefore used to shield the inner cones from the electric field and to allow the puffs of salt to get well mixed with the flame before entering the field. The tube, AA′, also served to greatly steady the flame. The flame is not affected by the field when the tube, AA′, and lower grating are used because it is practically uniform throughout the distance between the upper and lower gratings.
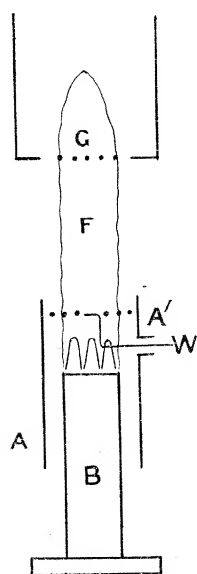
Since no deflexion of the puffs was obtained when using the lower grating and the tube, AA′, it appears that the luminous salt vapours in flames do not really move relatively to the flame in an electric field. I think the motion observed by LENARD, EBERT and ANDRADE was due to the deflexion of the flame which is difficult to estimate and allow for.

ANDRADE found $k = 0\cdot16$ cm. per second per volt per centimetre, which is about twenty times the upper limit given by the experiments just described, but agrees nearly with the value found when the lower part of the flame was not protected from the electric field. When the potential difference between the two gratings was increased sufficiently an arc formed accompanied by a great increase in the current. The arc could be seen to form a luminous streak down the flame, and the electrodes got very hot at each end of the arc and fused if the arc was allowed to continue for long. When an arc was formed the puffs of salt vapour became more brightly luminous and the coloration due to the salt could be seen, although faintly, all along the track of the arc. The position of the puffs was not changed when an arc formed. It appears, therefore, that positive ions move down the flame from the puffs when an arc is formed and form a small amount of luminous salt vapour in the arc. I think some positive ions are probably deflected downwards from the puffs, even when the field is not strong enough to arc, but they are not numerous enough to form visible vapour. In the arc the temperature is higher so that a smaller amount of salt vapour becomes perceptibly luminous.

PART II.—VELOCITY OF THE POSITIVE IONS OF SALT VAPOURS IN FLAMES.

Some new experiments on the velocity of the positive ions of salt vapours in flames will now be described.

The apparatus of the previous section with some modifications was used. The central part of the grating at the top of the tube, AA' (fig. 1), was removed and an insulated platinum wire electrode supported in the gap, so that the grating formed a guard ring round it. The wire supporting this electrode passed through a hole in the tube, AA', about 3 cm. from the top of it. This electrode was connected to a galvanometer, the other terminal of which was connected to the burner, B. The arrangement is shown in fig. 4. The upper grating electrode was connected to earth and the burner, B, was charged negatively. The galvanometer then indicated a small current passing down the flame from the upper grating to the electrode in the middle of the lower grating. Most of the current through the flame went to the guard ring and so was not indicated by the galvanometer. The potential gradient in the flame could be measured with the wire, PP', as before. The velocity of the flame was found with the puffs of salt vapour, but the puffs were not sent into the flame except when its velocity was being measured.

A bead of salt on a platinum wire could be introduced into the flame just below the upper grating, and the effect of the bead on the current through the galvanometer and on the potential gradient was determined. The distance between the upper and the lower gratings was about 7 cm.

It was found that putting in beads of lithium, sodium, potassium, rubidium, cæsium and strontium salts had no appreciable effect on the current or on the potential gradient below the bead with any potential difference from zero to 2700 volts. The potential gradient just below the bead was about 100 volts per centimetre when the P.D. used was 2700 volts. The velocity of the flame was 300 cm. per second. This shows that the positive ions from the beads did not move down the flame, even with the P.D. of 2700 volts, so that their velocities due to 1 volt per centimetre were less than 3 cm. per second.

The distance between the upper and lower gratings was then reduced to about 3 cm. It was then found that putting in a bead of any salt just below the upper electrode slightly increased the current and also slightly increased the potential gradient below the salt. The gradient in the salt vapour above the bead was very small, so that, since the salt vapour occupied about 1 cm. of the flame below the upper electrode, the effect of the salt was much the same as moving the electrodes 1 cm.

Fig. 4.

F, flame.
B, burner.
AA', tube round burner.
G, upper grating.
W, wire electrode.

nearer together. The increase in the current was about 25 per cent. with potentials up to 1800 volts. With 2700 volts the increase was larger, varying from 50 to 300 per cent. with different salts. This indicates that between 1800 and 2700 volts the positive ions began to move down the flame. If the salt beads were put into the flame about 1 cm. or 2 cm. below the upper grating, instead of close to it, an arc started with 2700 volts. Luminous salt vapour could be seen along the whole length of the arc.

The potential gradient below the beads of salt with potentials between 1800 and 2700 volts was about 300 volts per centimetre. Since the velocity of the flame was 300 cm. per second, this shows that the velocity of the positive ions was about 1 cm. per second for one volt per centimetre. The velocity was about the same for all salts, but could not be estimated accurately because the changes in the current due to putting in the beads increased gradually with the potential difference. It appears that the maximum velocity of the positive salt ions due to 1 volt per centimetre is not much greater than 1 cm. per second.

In the earlier experiments by the writer,* it was found that a bead of salt below the upper electrode began to increase the current at a P.D. of about 100 volts. Lusby† obtained a similar result and also found that the salt diminished the potential gradient below the bead. These results appear to have been due to a small amount of salt getting into the flame below the bead. This was prevented, in the experiments just described, by the chimney attached to the upper electrode. In the absence of the chimney, it was found that putting a bead below the upper electrode increased the current and diminished the potential gradient even with small potential differences· The salt vapour from the bead gets into the lower parts of the flame partly by circulating round with the air surrounding the flame inside the apparatus and partly by escaping into the air in the room and then entering the burner along with the air supply. The chimney entirely stopped both these processes. There was a strong draught up the chimney so that the salt vapour from the bead went straight up the chimney and did not get into the air surrounding the flame.

It appears that the earlier attempts to measure the velocity of the positive ions of salt vapours in flames gave values much too high. Andrade‡ has recently obtained values of about 3 cm. per second for 1 volt per centimetre for the positive ions of strontium salts. The difference between this and the value of about 1 cm. per second just obtained may be due partly to differences between Andrade's flames and mine. Also there may have been a few positive ions, even in my flames, with velocities greater than 1 cm. per second.

When a large increase in the current is produced by putting in the bead an arc forms as already mentioned. The potential gradient necessary to start an arc was

* 'Phil. Trans.,' A, vol. 192, p. 499, 1899.
† 'Proc. Camb. Phil. Soc.,' vol. xvi., Pl. 1, 1910.
‡ *Loc. cit.*

rather greater than 300 volts per centimetre. I think, when any great number of positive ions moves down to the negative electrode an arc starts because the positive ions form salt vapour by recombining with negative ions, and the salt diminishes the drop of potential at the negative electrode and so increases the gradient between the electrodes. The gradient required for an arc to start on putting in a bead of salt is, therefore, probably that required to make a large number of positive salt ions move down the flame. According to the earlier experiments all salts give positive ions having equal velocities. This conclusion is probably correct in spite of the large error made in the absolute value of the velocity. The salt vapour really extended down the flame nearly to the lower electrode and was not confined to the part of the flame close to the bead as was supposed. The potential gradient which made the ions move down was therefore the gradient just above the lower electrode and not that just below the bead. This explanation of the large velocities obtained in the earlier experiments was suggested by ANDRADE. The present experiments have convinced me that his suggestion is correct.

PART III.—RELATION BETWEEN LUMINOSITY AND CONDUCTIVITY OF SALT VAPOURS IN FLAMES.

Some experiments on the changes in the luminosity and conductivity of flames containing sodium chloride, due to the addition of chloroform, will now be described.

A mixture of air, spray of a sodium chloride solution and gasoline vapour produced by a sprayer was passed through a T-tube into two similar burners. The tube to one of the burners led the mixture through a vessel in which chloroform could be placed.

The luminosities of the two flames were compared by means of a Hilgers' spectro-photometer.

Each flame contained two platinum electrodes separated by a horizontal distance of about 8 cm. A current from a battery of from 10 to 300 cells could be passed between these electrodes. In each flame two fine platinum wires were introduced about 5 cm. apart, and either pair could be connected to a quadrant electrometer. These wires were horizontal and perpendicular to the horizontal line joining the centres of the electrodes between which the current was passed.

The current between the electrodes was measured with a galvanometer, and the ratio of the current to the potential difference between the fine wires was taken as a measure of the conductivity. When no chloroform was used the two flames had equal conductivities and luminosities.

The following table contains the results obtained :—

Solution in sprayer (grammes NaCl per litre).	Ratio of conductivities (without $CHCl_3 \div$ with $CHCl_3$).	Ratio of luminosities (without $CHCl_3 \div$ with $CHCl_3$).
0	8·0	1·9
0·8	5·7	2·1
4	6·0	1·9
20	6·1	1·9
200	6·0	1·9

It appears that for all concentrations of the sodium chloride the chloroform diminished the conductivity about six times, and the luminosity about two times.

It was found that the chloroform increased the current through the flame, although it diminished the conductivity. The current depends on the conductivity throughout the volume of the flame and on the resistance close to the negative electrode. The flame, away from the negative electrode, obeys OHM's law, but at the negative electrode there is a large fall of potential which is approximately proportional to the square of the current. The chloroform increased the current from four to ten times. Since the conductivity, measured by the ratio of the current to the potential gradient between the two wires, was diminished, it follows that the chloroform must have considerably diminished the fall of potential at the negative electrode.

If potassium carbonate is put on the negative electrode the fall of potential there almost disappears, and then the current depends on the conductivity of the rest of the flame. It was found that with potassium carbonate on the negative electrode the chloroform decreased the current about six times in agreement with the change in the conductivity. The effect of the chloroform on the temperature of the flame was measured with a thermocouple. It was found that the temperature of the couple was changed from about 1650° C. to 1600° C.

If the current through the flame had been taken as a measure of its conductivity a large increase in the conductivity accompanied by a diminution of the luminosity would have been found.
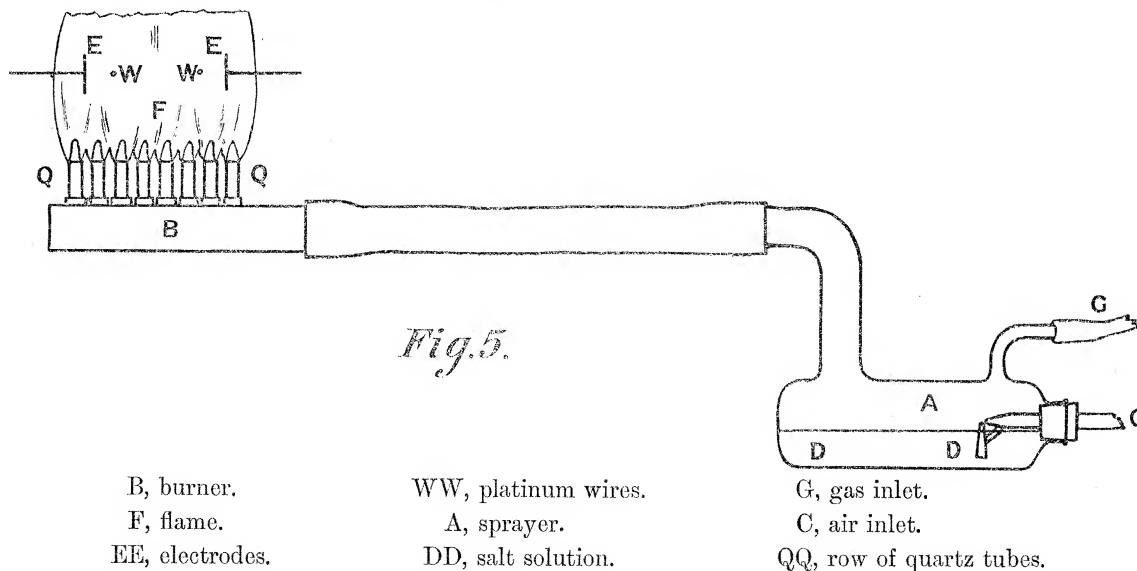
The relation between the potential difference used to send a current through a flame between clean platinum electrodes and the current is represented by the equation
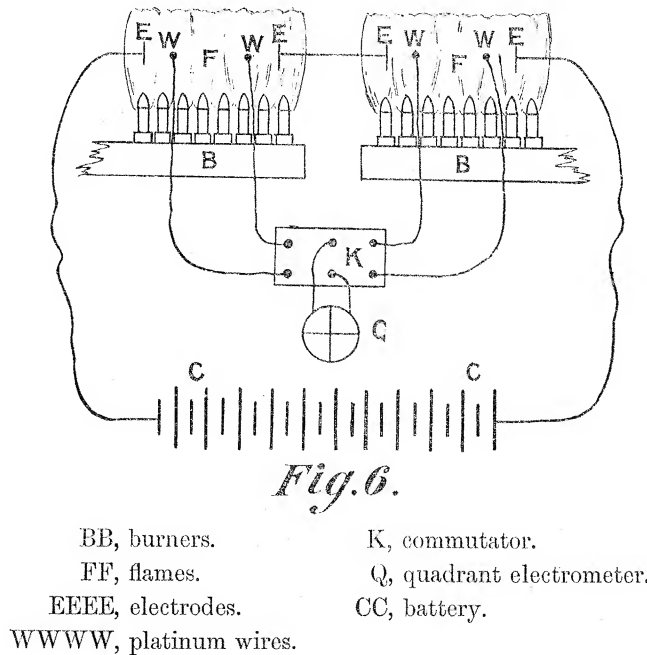
$$V = Acd + Bc^2.$$

Where V denotes the P.D., c the current, d the distance between the electrodes, and A and B are constants. The term Bc^2 represents the fall of the potential at the negative electrode, and the term Acd the fall of potential in the uniform gradient between the electrodes. It appears that the chloroform diminishes B but increases A.

With small potentials and currents the term Acd is relatively more important, so that the chloroform then should decrease the current, while with large potentials the term Acd becomes negligible and then the chloroform increases the current.

In the experiments of SMITHELLS, DAWSON, and the writer* it was found that chloroform diminished the current with very small potentials but increased it with

Fig.5.

B, burner.	WW, platinum wires.	G, gas inlet.
F, flame.	A, sprayer.	C, air inlet.
EE, electrodes.	DD, salt solution.	QQ, row of quartz tubes.

larger potentials.   The potentials used in the present experiments were large and the chloroform increased the current.

Fig.6.

BB, burners.	K, commutator.
FF, flames.	Q, quadrant electrometer.
EEEE, electrodes.	CC, battery.
WWWW, platinum wires.	

It is clear that the current is not a measure of the conductivity, but the ratio of the current to the uniform electric intensity away from the negative electrode is proportional to the true conductivity of the flame.

* 'Phil. Trans.,' A, vol. 193, p. 89, 1899.

Experiments on the variation of the conductivity and luminosity with the concentration of the salt vapour in the flame will now be described. Two similar and equal sprayers were used, supplying a mixture of air, gas and spray, to two equal burners. The sprayers were adjusted so that when both contained the same solution the two flames had equal conductivities and luminosities. The electrodes in the two flames were connected in series so that the same current passed through each flame. The uniform potential gradients in the flames were then inversely proportional to their conductivities. Fig. 5 shows one of the burners and its sprayer. Fig. 6 shows the two flames and the electrical connections. The luminosities were compared with the spectrophotometer.

The following table contains the results obtained with solutions of sodium chloride :—

Solutions sprayed (grammes NaCl per litre).		Ratio of conductivities.	Ratio of luminosities.
Flame A.	Flame B.	A/B.	A/B.
20	20	1·00	1·00
20	4	2·21	2·14
20	0·8	5·00	4·62
20	0·16	9·00	9·75
20	0	33·3	36·7
4	0·8	2·26	2·16
0·8	0·16	2·40	2·11
0·16	0·032	1·70	2·90

It appears that both the luminosity and conductivity are roughly proportional to the square root of the concentration of the sodium chloride in the flame. It was shown by GOUY* that the luminosity is nearly proportional to the square root of the concentration.

The following results were obtained with sodium carbonate solutions :—

Solutions sprayed (grammes Na_2CO_3 per litre).		Conductivities.	Luminosities.
Flame A.	Flame B.	A/B.	A/B.
18·12	18·12	1	1
18·12	1·812	3·1	2·9
18·12	0·1812	9·8	8·6

* 'Ann. Chim. et Phys.,' (5), 18, pp. 5–101 (1879).

It appears that the conductivity and luminosity due to the sodium carbonate are nearly proportional to the square root of the concentration as with sodium chloride. The following results were obtained :—

Solutions sprayed (grammes per litre).		Conductivities.	Luminosities.
Flame A. NaCl.	Flame B. Na$_2$CO$_3$.	A/B.	A/B.
200	181·2	1·00	1·00
20	18·12	1·00	1·00
2	1·812	1·00	1·00
0·2	0·1812	1·00	1·00

It appears that the conductivities and luminosities of sodium chloride and sodium carbonate in any chemically equivalent quantities are equal.

The luminosity due to a sodium chloride solution containing 20 gr. per litre was found to be equal to that due to a solution containing 20 gr. of sodium chloride and 200 c.c. of strong hydrochloric acid per litre. Thus an excess of HCl does not affect the luminosity due to NaCl. This agrees with the conclusion that the effect of CHCl$_3$ on the luminosity due to NaCl is due to the change in the character of the flame and not to chemical action.

It was found that the sodium light luminosity due to a solution containing 18·12 gr. Na$_2$CO$_3$ per litre was equal to that due to a solution containing 18·12 gr. Na$_2$CO$_3$, and 23·6 gr. K$_2$CO$_3$ per litre. The conductivity due to the solution containing K$_2$CO$_3$ was about nine times that due to the one containing only Na$_2$CO$_3$. The negative ions from the K$_2$CO$_3$ must have diminished the number of positive sodium ions nine times, so that this result agrees with the conclusion that sodium light is not due to positive ions.

PART IV.—THE RELATION BETWEEN THE CONDUCTIVITY AND THE CONCENTRATION OF SALT VAPOURS IN FLAMES.

The earlier experiments of ARRHENIUS[*] and of SMITHELLS, DAWSON and the writer[†] showed that the current is nearly proportional to the square root of the concentration when the concentration is small. SMITHELLS, DAWSON and the writer found that with larger concentrations the current due to oxysalts increases much more rapidly than as the square root of the concentration. In all these earlier

* 'Wied. Ann.,' vol. xliii., p. 18, 1891.
† 'Phil. Trans.,' A, vol. 193, p. 89, 1899.

experiments the current, due to a constant P.D., between two platinum electrodes near together in the flame, was taken as a measure of the conductivity.

The relation $V = Acd + Bc^2$ shows that when the electrodes are near together and the term Acd therefore small, the current depends mainly on the fall of potential at the negative electrode which is represented by Bc^2.

The conductivity of the flame in the uniform potential gradient between the electrodes has little influence on the current when the electrodes are near together.

It seemed likely that measurements of the conductivity, as measured by the ratio of the current to the uniform potential gradient, away from the negative electrode, might give simpler and more easily interpreted results than those previously obtained.

The apparatus described in the preceding section of this paper was used. The same current was passed through two similar flames and the ratio of the uniform potential gradients in them measured. The amount of salt in one flame was kept constant and that in the other varied. In this way the ratios of the conductivities of the second flame, with different amounts of salt in it, were found. The first flame merely served as a standard with which to compare the second one. It was not assumed that the two flames had equal conductivities when solutions of equal strength were sprayed into them, although this was roughly true. Variations in the gas and air supplies probably affected both flames nearly equally, and therefore had little effect on the results obtained.

The following results were obtained with solutions of cæsium chloride :—

Solutions sprayed (grammes CsCl per litre).		Ratio of conductivities.
Flame A.	Flame B.	B/A.
20·2 (RbCl)	80	3·13
20·2 (RbCl)	8	1·00
20·2 (RbCl)	0·8	0·301
0·08	0·016	0·535
0·08	0·032	0·813
0·08	0·08	1·37
0·08	0·16	1·92
0	0	1·00
0	0·0032	2·88
0	0·008	5·72
0	0·016	8·90
0·8	0·8	0·75
0·8	0·08	0·21

The following tables gives the conductivities of the flame containing different amounts of CsCl, deduced from the above results, taking that of the flame without salt equal to unity :—

Solution sprayed (grammes CsCl per litre).	Conductivity.
0	1
0·0032	2·88
0·008	5·72
0·016	8·9
0·032	13·5
0·08	22·7
0·16	32·8
0·8	85·2
8·0	282
80	883

The ionic theory of the variation of the conductivity with the concentration will now be considered.

Let S denote the number of salt molecules per cubic centimetre in the flame, ionised or not, and n the number of positive salt ions per cubic centimetre. Then $S-n$ will be the number of non-ionised salt molecules if we suppose one salt molecule gives one positive ion.

Let F denote the number of flame molecules per cubic centimetre, which can be ionised, and m the number of flame-positive ions per cubic centimetre, $F-m$ is then the number of non-ionised flame molecules per cubic centimetre.

We then have

$$S-n = \alpha n\,(n+m). \qquad \ldots \ldots \ldots \ldots \quad (1)$$

$$F-m = \beta m\,(n+m), \qquad \ldots \ldots \ldots \ldots \quad (2)$$

where α and β are constants; α is the ratio of the coefficient of recombination of the positive salt ions with the negative ions to the fraction of the non-ionised salt molecules which ionise per second; β is the same thing for the flame-positive ions. F is very large compared with S, and m is usually small compared with n. Hence m must be extremely small compared with F, so that $F-m$ may be replaced by F.

The conductivity (c) of the flame is proportional to the total number of ions per cubic centimetre, so that

$$Ac = n+m, \qquad \ldots \ldots \ldots \ldots \ldots \quad (3)$$

where A is a constant.

Replacing $F-m$ by F and eliminating n and m from (1), (2), and (3), we obtain

$$\frac{S}{1+\alpha Ac} + \frac{F}{\beta Ac} = Ac.$$

If we take $c = 1$ when $S = 0$ this becomes

$$\frac{S}{1+\alpha Ac} = Ac - \frac{A}{c}$$

or

$$S = A\frac{c^2-1}{c}(1+\alpha Ac). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When c is large this reduces to

$$S = \alpha A^2 c^2.$$

Since all salts give ions having the same velocities in the flame, it follows that the constant A should have the same value for all salts. The equation (4), therefore, only contains one constant (α) which varies with the nature of the salt.

The fraction of the salt molecules which are ionised is given by

$$\frac{n}{S} = \frac{1}{1+\alpha Ac}.$$

Let k denote the concentration in grammes per litre of the solution sprayed into the flame, and let $GS = 10^4 k$, where G is a constant proportional to the molecular weight of the salt.

We have then

$$10^4 k = GA\left\{\frac{c^2-1}{c}\right\}(1+\alpha Ac).$$

When c is large suppose $10^4 k = ac^2$, so that $a = G\alpha A^2$, and let $b = GA$, so that

$$10^4 k = \frac{c^2-1}{c}(b+ac). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\frac{n}{S} = \frac{b}{b+ac}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The equation (5) agrees with the values of c found for cæsium chloride within the limits of experimental error if $b = 10$ and $a = 1$. The following table gives the

values of $10^4 k$ calculated from (5), using the observed values of c. The calculations were done with a slide rule :—

c.	k (calculated).	k (experimental).
1	0	0
2·88	0·00326	0·0032
5·72	0·0087	0·008
8·9	0·0166	0·016
13·5	0·0315	0·032
22·7	0·074	0·08
32·8	0·14	0·16
85·2	0·81	0·8
282	8·2	8·0
883	79·0	80·0

The experimental numbers for c are probably reliable to about 5 per cent., so that when k is calculated from c the results may be in error by 10 per cent.

The calculated and experimental values of k agree to less than 10 per cent. in nearly all cases. When the enormous variation in k, from 0·0032 to 80, is taken into account, it may be said that the results are in good agreement with the ionic theory.

Since

$$\frac{n}{S} = \frac{b}{b+ac},$$

we get for cæsium chloride

$$\frac{n}{S} = \frac{10}{10+c}.$$

The following table gives the percentage of the CsCl molecules, which are ionised in the flame according to this equation :—

Solution sprayed (grammes CsCl per litre).	$\frac{n}{S} \times 100$.
0	90·9
0·0032	75·6
0·032	41·8
0·16	22·0
0·8	10·6
8·0	3·5
80·0	1·1

The salt vapour is not completely ionised when its concentration is extremely small, because of the finite number of flame ions present with which the salt ions can recombine.

PART V.—THE RELATIVE CONDUCTIVITIES OF SALTS OF DIFFERENT ALKALI METALS.

The relative conductivities of salts of different metals were determined with the apparatus described in Section III. The two flames were adjusted so that they had equal conductivities when the same solution was sprayed into them.

It was found that when the concentrations were large the conductivity was nearly proportional to the square root of the concentration with all salts. Results proving this to be true will be given later in this section. It follows that the ratio of the conductivities of any two salts, at equal concentrations, is independent of the concentration provided the concentration is large.

The following table gives the results obtained :—

Solutions sprayed (grammes per litre).		Ratio of conductivities.
Flame A.	Flame B.	B/A.
$18 \cdot 12 \ Na_2CO_3$	$23 \cdot 6 \ K_2CO_3$	$9 \cdot 3$
$18 \cdot 12 \ Na_2CO_3$	$25 \cdot 6 \ KCl$	$9 \cdot 3$
$25 \cdot 6 \ KCl$	$20 \cdot 2 \ RbCl$	$0 \cdot 89$
$8 \ CsCl$	$20 \cdot 2 \ RbCl$	$0 \cdot 89$

The following table gives the relative conductivities, at large concentrations, of the salts of different metals for concentrations such that equal numbers of metal atoms are present in the flame in each case. The conductivity for sodium salts is taken equal to unity :—

Salt.	Relative conductivities.
NaCl	1
Na_2CO_3	1
KCl	$9 \cdot 3$
K_2CO_3	$9 \cdot 3$
RbCl	$11 \cdot 8$
CsCl	$25 \cdot 02$

These numbers were calculated from the relative conductivities given in the previous table. It was shown in Section III. that NaCl and Na_2CO_3 have equal conductivities when present in chemically equivalent amounts.

<div align="center">M 2</div>

The following table gives the relative concentrations (proportional to metal atoms per unit volume) for which the conductivities are equal. These numbers are also only correct for large concentrations. The concentration is taken as unity in the case of cæsium :—

Metal.	Atomic weight.	Concentration.
Na	23	626·0
K	39	7·25
Rb	85	4·48
Cs	133	1·00

The equation $10^4 k = \dfrac{c^2 - 1}{c}(b + ac)$, which was found to represent the results obtained with cæsium chloride, can be applied to the other salts also.

The constant a is proportional to the large concentrations in grammes per litre which give equal conductivities. The constant b has the same value for all salts when the concentrations are taken proportional to the number of metal atoms in unit volume. When the concentrations are expressed in grammes per litre b is proportional to the molecular weight of the salt actually present in the flame. Since chlorides and carbonates give equal conductivities it is probable that chemically equivalent amounts give equal numbers of salt molecules in the flame. Probably the carbonates and chlorides are decomposed into oxides. The constant b for alkaline carbonates is therefore probably proportional to one-half their molecular weights.

The following table gives the values of a and b calculated in this way so as to give k in grammes per litre in the solution sprayed into the flame :—

Salt.	a.	b.
NaCl	217·00	3·47
Na_2CO_3	197·00	3·14
KCl	3·20	4·42
K_2CO_3	3·0	4·10
RbCl	3·20	7·20
CsCl	1·00	10·00

The following is an example of the method used for calculating the above constants. For RbCl we have

$$a = 1 \times 4\text{·}48 \times \frac{121}{168\text{·}5} = 3\text{·}2.$$

Here 1 is the value of a for cæsium chloride, 4·48 is the equivalent large concentration at which rubidium salts have conductivities equal to cæsium salts at the large concentration unity, 121 is the equivalent weight of RbCl, and 168·5 that of CsCl. Also for RbCl

$$b = 10 \times \frac{121}{168 \cdot 5} = 7 \cdot 20$$

where 10 is the value of b found for CsCl.

To see if the equation $10^4 k = \dfrac{c^2-1}{c}(b+ac)$ would give results agreeing with experimental values, using the values of a and b given above, a number of measurements of the relative conductivities at small concentrations were made.

The following results were obtained with solutions of RbCl :—

Solutions sprayed (grammes RbCl per litre).		Ratio of conductivities.
Flame A.	Flame B.	B/A.
0·0202	0	0·178
0·0202	0·00202	0·34
0·0202	0·0202	1·30
0·0202	0·202	4·32

Taking the conductivity when spraying water equal to unity, these results give the following numbers :—

Solution sprayed (grammes RbCl per litre) (k).	Conductivity (found).	k (calculated).
0	1	0
0·00202	1·91	0·0019
0·0202	7·30	0·0219
0·202	24·2	0·202

The last column contains the values of k given by the equation

$$10^4 k = \frac{c^2-1}{c}(7 \cdot 2 + 3 \cdot 2c).$$

The following results were obtained with potassium carbonate :—

Solution sprayed (grammes K_2CO_3 per litre).		Ratio of conductivities.
Flame A.	Flame B.	B/A.
0·0236	0	0·164
0·0236	0·00236	0·338
0·0236	0·0236	1·300
0·0236	0·236	4·59
2·36	0·236	4·61
2·36	2·36	1·39

Taking C = 1 when k = 0, these results give the following values :—

Solution sprayed (grammes K_2CO_3 per litre) (k).	Conductivity (found).	k (calculated).
0	1	—
0·00236	2·07	0·00164
0·0236	7·98	0·0221
0·236	28·0	0·246
2·36	84·6	2·18

The numbers in the third column are those given by the equation

$$10^4 k = \frac{c^2 - 1}{c} (4\cdot1 + 3c).$$

In Section III. the relative conductivities of several sodium chloride solutions are given. The following table gives numbers calculated from those results taking $c = 30\cdot3$ when $k = 20$ gr. per litre. The value $c = 30\cdot3$ when $k = 20$ was got from the relative conductivities found for cæsium and sodium salts :—

Solution sprayed (grammes NaCl per litre) (k).	Conductivity (found).	k (calculated).
20	30·3	19·9
4	13·7	4·05
0·8	6·06	0·79
0·16	2·95	0·168
0·032	1·73	0·044

The last column contains numbers given by the equation $10^4k = \dfrac{c^2-1}{c}(3\cdot 5 + 217c)$.

The following table gives the percentage of the salt molecules ionised when k is very small so that $c = 1$. These numbers were calculated by means of the equation

$$\frac{n}{S} = \frac{b}{b+ac},$$

putting $c = 1$.

Salt.	$\dfrac{n}{S} \times 100.$
NaCl	1·6
Na$_2$CO$_3$	1·6
KCl	58·0
K$_2$CO$_3$	58·0
RbCl	69·0
CsCl	90·9

The ionization is not complete when the concentration of the salt vapour is very small because of the finite number of flame ions present with which the salt ions can recombine.
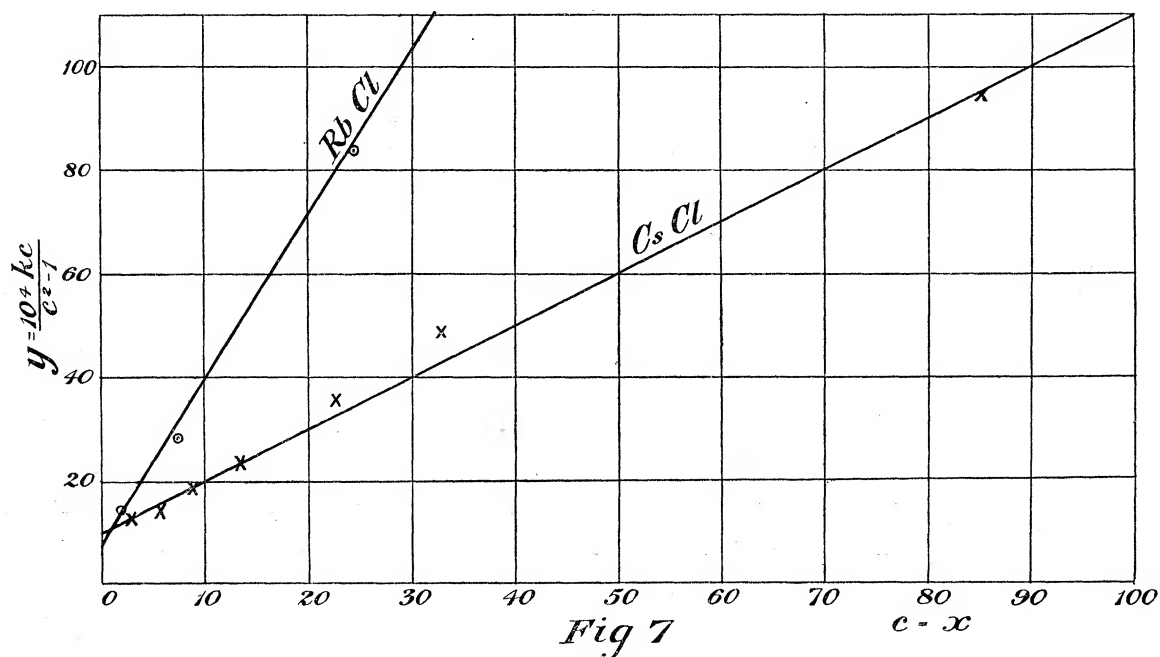
Fig 7

The equation $10^4k = \dfrac{c^2-1}{c}(b+ac)$ shows that $\dfrac{10^4kc}{c^2-1}$ is a linear function of c. Fig. 7 shows graphically the relation between the experimental values of $\dfrac{10^4kc}{c^2-1}$ and c for

CsCl and RbCl. The straight lines are those given by the equation $y = b + ac$. The crosses representing the experimental results fall nearly on the straight lines. Fig. 8 and fig. 9 show the same thing for K_2CO_3 and NaCl. In the case of NaCl the straight line passes practically through the origin but with the other salts it is clear that this is not the case. The larger values of c and $\dfrac{10^4 kc}{c^2 - 1}$ are not shown. They were used to calculate the constant a and so, of course, the points representing them would fall on the straight lines given by $y = b + ac$ since b becomes negligible when c is large.

If a solution containing two or more salts is sprayed into the flame, then, since the

Fig 8
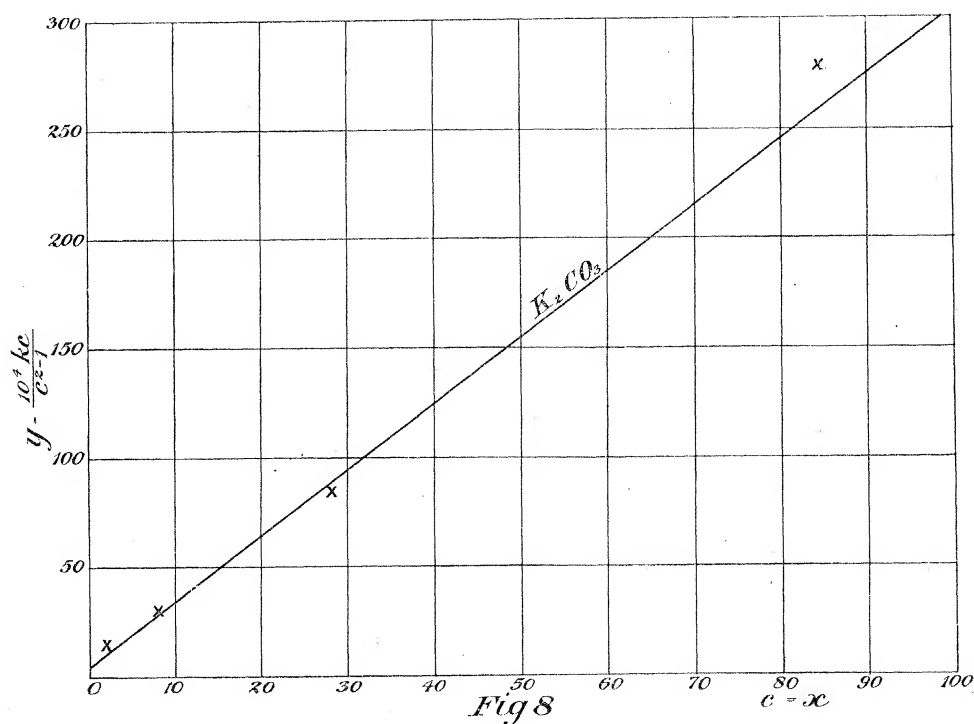
ions from one salt can combine with the ions from the other, the conductivity should not be equal to the sum of the conductivities due to equal amounts of each salt alone.

Let there be S molecules of one salt and S′ of the other present per cubic centimetre in the flame. Let the first salt produce n positive ions per cubic centimetre, and the second n'. We have

$$S - n = an(n + n' + m),$$

$$S' - n' = a'n'(n + n' + m),$$

$$F = \beta m(n + n' + m),$$

$$Ac = n + n' + m.$$

Here F, m and β relate to the flame as before. These equations give

$$A\frac{c^2-1}{c} = \frac{S}{1+\alpha A c} + \frac{S'}{1+\alpha' A c}$$
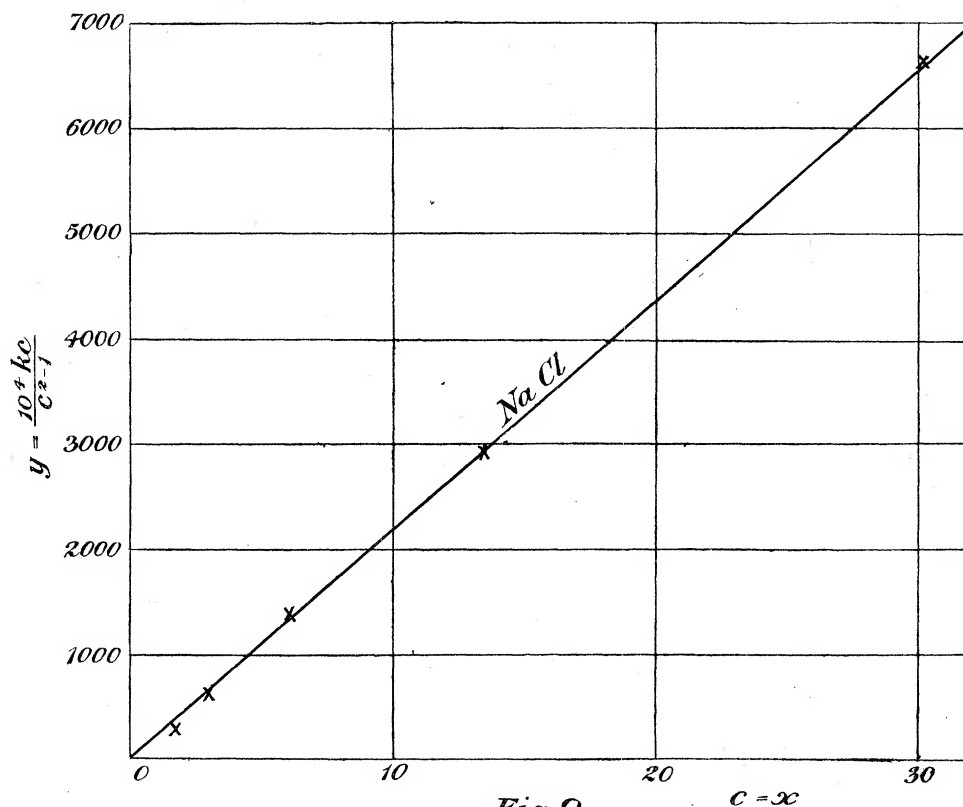
where c is taken equal to unity when

$$S = S' = 0.$$

Fig 9.

Let $10^4k = GS$, $10^4k' = G'S'$, $b = GA$, $b' = G'A$, $a = G\alpha A^2$, and $a' = G'\alpha' A^2$, so that

$$\frac{c^2-1}{c} = \frac{10^4k}{b+ac} + \frac{10^4k'}{b'+a'c}.$$

To test this equation the conductivity, due to a solution of 9·06 gr. Na_2CO_3 and 0·164 gr. K_2CO_3 in a litre, was compared with that due to a solution of 18·12 gr. of Na_2CO_3 in a litre. The first solution gave a conductivity equal to 1·06 times that of the second. For the second solution $c = 30·3$, so that c for the mixture was 32·2. The above equation gives $c = 31·55$. The sum of the conductivities due to the Na_2CO_3 and K_2CO_3 when not mixed is 44·6.

PART VI.—SUMMARY OF RESULTS AND CONCLUSION.

The chief results obtained are as follows :—

(1.) The luminous vapours of salts in a Bunsen flame are not deflected appreciably by an electric field.

(2.) The positive ions present in the luminous vapour can be made to move out of it by an electric field.

(3.) The positive ions are not luminous, but can form luminous vapour after recombination.

(4.) The velocity of the positive salt ions in flames is about 1 cm. per second for 1 volt per centimetre and is the same for all salts.

(5.) The conductivity and luminosity of sodium chloride both vary nearly as the square root of the concentration of the salt vapour in the flame.

(6.) The conductivities and luminosities of chemically equivalent amounts of sodium chloride and sodium carbonate are equal.

(7.) A considerable excess of hydrochloric acid does not change the luminosity due to sodium chloride and slightly increases the conductivity of the flame.

(8.) A large excess of hydrochloric acid obtained by the introduction of chloroform vapour diminishes the luminosity due to NaCl about 50 per cent., and diminishes the conductivity about six times. The percentage changes in the luminosity and conductivity are independent of the concentration of the NaCl vapour.

(9.) The $CHCl_3$ increases the current due to large potential differences, but diminishes the conductivity as measured by the ratio of the current to the uniform potential gradient in the flame.

(10.) When the drop of potential at the negative electrode is got rid of by putting K_2CO_3 on it, the $CHCl_3$ diminishes the current to about the same extent as the conductivity.

(11.) The presence of a large amount of K_2CO_3 does not change the luminosity due to Na_2CO_3, although the K_2CO_3 greatly increases the total conductivity.

(12.) The variation of the conductivity (c) with the concentration (k) for alkali salts can be represented by the equation $10^4 k = \dfrac{c^2-1}{c} (b+ac)$, using proper values of the constants a and b for each salt.

(13.) The equation $10^4 k = \dfrac{c^2-1}{c} (b+ac)$ can be deduced from the ionic theory and the fraction of the salt molecules which are ionised is equal to $b/(b+ac)$.

(14.) Alkaline chlorides and carbonates impart equal conductivities to the flame for chemically equivalent concentrations.

(15.) The percentage of the salt which is ionised when the concentration is very small has the following values :—

Cæsium salts	91
Rubidium salts	69
Potassium salts	58
Sodium salts	1˙6

(16.) The constant, b, is proportional to the molecular weight of the salt. According to the theory this shows that all salts give negative ions having the same velocity due to an electric field.

(17.) The conductivity due to solutions containing a mixture of salts agrees with that to be expected on the ionic theory.

It is probable that the luminous salt vapours are not appreciably moved by an electric field because very few of the salt molecules which become luminous, while the salt passes through the flame, also get ionised.

If f denotes the fraction of the salt molecules which are ionised in the flame at any instant, then fkX will be the average velocity of a salt molecule over a long time due to an electric field. Now f for sodium is very much smaller than for cæsium, yet both give positive ions, having about the same velocity. We conclude, therefore, that the ionic velocities observed are not of the values of fkX, but the maximum possible velocities kX. It follows that when a salt molecule ionises, the ions sometimes last long enough for their velocity to be measured before they recombine. The method used to measure the ionic velocities indicates the maximum velocities, not the average velocity for a large number of ions.

According to the most recent theories of ionic velocity, the velocity depends chiefly on the nature of the gas in which the ions move, and not much on the mass of the ions. We should, therefore, expect k to be about the same for ions of different salts all moving in the same flame.

The fact, first discovered by GOUY and here confirmed, that the luminosity due to sodium salts varies nearly as the square root of the concentration indicates that the luminous molecules are produced by a binary reaction from the sodium salt.

If the luminosity is due to atoms of sodium, a possible reaction is $Na_2O + CO = 2Na + CO_2$.

CO and CO_2 are both present in large quantities in the flame, so that their concentrations may be regarded as constants, and therefore the concentration of the Na will vary as the square root of the concentration of the Na_2O. Probably nearly all the salt is converted into Na_2O in the flame so that the concentration of the salt is proportional to the concentration of the Na_2O, when the concentration is not very small.

It seems probable that adding HCl to the flame does not prevent the conversion of NaCl into Na_2O by the flame gases. Otherwise, HCl should diminish the

luminosity by an amount depending on the ratio of the concentration of the sodium to the concentration of the HCl. It appears that the reaction $Na_2O + 2HCl = 2NaCl + H_2O$ does not proceed appreciably at the temperature of the flame. The small effect which the HCl has on the luminosity is probably due to the change in the temperature of the flame together, possibly, with other causes.

The effect of the HCl on the conductivity was also independent of the ratio of the concentrations of the sodium and HCl. It follows, as for the luminosity, that the effect must be due to the change in the nature of the flame produced by the HCl and not to chemical action of the HCl on the sodium salts. Possibly the HCl condenses on the negative ions, so diminishing their velocity.

The effect of the HCl on the fall of potential at the negative electrode may be due to its causing the electrode to emit negative electrons.

In the earlier experiments of SMITHELLS, DAWSON, and the writer, it was found that at large concentrations oxysalts gave greater currents than haloid salts. The present experiments show that the conductivity is the same for haloid and oxysalts at all concentrations. It follows that the oxysalts diminish the fall of potential at the negative electrode when present in large quantities, while the haloid salts do not do so to the same extent. The amount of salt which entered the flame in the present experiments was rather greater than in the earlier experiments, for solutions of equal concentration.

The present experiments on the variation of the conductivity with the concentration can be explained in a satisfactory way on the ionic theory, and they confirm the view that all salts give negative ions, having equal velocities in the flame.

The fact that K_2CO_3 does not diminish the luminosity due to Na_2CO_3 seems to show conclusively that the luminosity is not due to positive ions. The K_2CO_3 increased the number of negative ions about nine times, and, therefore, must have diminished the number of positive sodium ions in the same ratio. That the negative ions from K_2CO_3 do combine with the positive ions from Na_2CO_3 is shown by the fact that the conductivity of a mixture of sodium and potassium carbonates is less than the sum of their separate conductivities as it should be according to the ionic theory.

In conclusion, I wish to say that my thanks are due to the trustees of the Rice Institute for the facilities for experimental work which they have provided.